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(21) International Application Number: PCT/EP94/01532 (22) International Filing Date: 10 May 1994 (10.05.94) (30) Priority Data: 93870079.6 13 May 1993 (13.05.93) EP <i>(34) Countries for which the regional or international application was filed:</i> AT et al. (71) Applicant (for all designated States except US): INTERUNI- VERSITAIR MICROELEKTRONICA CENTRUM [BE/BE]; Vereniging Zonder Winstbejag, Kapeldreef 75, B-3001 Heverlee (BE). (72) Inventors; and (75) Inventors/Applicants (for US only): VERHAVERBEKE, Steven [BE/BE]; J. Lebrunstraat 2/B6, B-1040 Schaar- beek (BE). GEUSENS, Walda [BE/BE]; Nieuwstraat 42, B-3360 Korbeek-Lo (BE). BELLEMANS, Marc [BE/BE]; Sparrenhof 7, B-3071 Erps-Kwerps (BE). DULST, Marc [BE/BE]; Kerkstraat 148, B-1150 Sint-Pieters-Woluwe (BE). MEURIS, Marc [BE/BE]; D. Liekenslaan 27, B-3140 Keerbergen (BE). HEYNS, Marc [BE/BE]; Merelnest 14, B-3210 Linden (BE).		(74) Agents: VAN MALDEREN, Joëlle et al.; Office Van Malderen, Place Reine Fabiola 6/1, B-1080 Bruxelles (BE). (81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHOD FOR SEMICONDUCTOR PROCESSING USING MIXTURES OF HF AND CARBOXYLIC ACID (57) Abstract <p>Method for semiconductor processing comprising etching of oxide layers, especially etching thick SiO₂ layers and/or last step in the cleaning process wherein the oxide layers are treated in the liquid phase with a mixture of hydrogen fluoride and one or more carboxylic acids, possibly in admixture with water. The spent solution may be reprocessed to recover the carboxylic acid over ion exchange resins.</p>		

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METHOD FOR SEMICONDUCTOR PROCESSING USING MIXTURES OF HF AND CARBOXYLIC ACID

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Objects of the present invention

The present invention is related to improvements in semiconductor processing using HF formulated mixtures. The invention is more specifically related to methods making use of these mixtures in liquid phase etching techniques of oxide layers, especially etching thick SiO_2 layers and in the so-called last step in the cleaning process. The specific composition of the HF formulated mixtures of the present invention allows also reprocessing of these mixtures and the present invention extends to a reprocessing method of such mixtures.

State of the art and background of the invention

In the semiconductor processing, HF mixtures are often used for etching thick SiO_2 layers or for etching chemical oxide layers.

For etching thick SiO_2 layers, usually buffered HF is used, which is a mixture of NH_4F and HF, in the liquid phase, generally as a solution in water.

Moreover, as a last step in the cleaning process, usually a diluted HF step is used.

It is generally recognized that it is difficult to control the etching reaction of SiO_2 with hydrogen fluoride and to apply the etching process with good repeatability.

Moreover, the treated substrate surface may not be contaminated by ions or particles, lest various defects of the product are liable to occur.

Etching of bare silicon wafers in HF solution and/or a final etch in HF solution generally in combination with the RCA-process have been the object of many experimentation and publications.

5 The RCA-cleaning process for bare or oxidized silicon wafers is based on a two-step oxidizing and complexing treatment with hydrogen peroxide solutions: an alkaline mixture at high pH and followed by an acidic mixture at low pH (W. Kern and D. Puotinen, "Cleaning Solutions Based
10 on Hydrogen Peroxide for Use in Silicon Semiconductor Technology", RCA Review, 31, 187-206 (1970)).

"HF-last cleaning" result in a passivated Si-surface with a low metallic contamination which is, however, very susceptible to contamination. A silicon surface that has
15 been exposed to HF is highly reactive and immediately attracts particles and organic contaminants from solution, D.I. water, and ambient air. HF-last processing before gate oxidation is, therefore, still a point of controversy.

Regarding treatment, before Si-epitaxy, the same
20 controversy exists.

Recently, a combination of the two methods was proposed as a pre-clean before Si-epitaxy which, however, still requires temperatures up to 880°C in the pre-treatment. (A.J. Pidduck et al., Proc. 2nd Int. Symp. on Cleaning Tech-
25 nology in Semiconductor Device Manufacturing, 180th Electrochem. Soc. Meeting (Phoenix, 1991)).

Document US-4395304 describes a selective chemical etchant solution for phosphosilicate glass (PSG).

Document EP-A-0438727 describes a process and
30 solution for liquid treatment of semiconductor surfaces in order to reduce particulate contamination. This aims is obtained with the use of an acid.

Aims of the present invention

The main aims of the present invention are to
35 provide HF formulated mixtures operating in the liquid phase which are more reliable than previous mixtures and which have an etching behavior which is very reproducible, which provide good surface tension properties and good electrical results

in respect of the oxides grown on oxide stripped silicon surfaces, which improves the solubility of metallic impurities such as Ca^{++} and reduces particulate contamination compared to conventional techniques.

5 Since the environmental restrictions on waste chemicals become more and more stringent, a further aim of the present invention is to provide reprocessable mixtures, thus reducing substantially the pollution due to waste mixtures.

10 Another aim is to provide HF formulated mixtures which are equally suitable for etching processes and cleaning processes, especially last step cleaning operations.

 Of course, the precise composition must be adapted, especially in respect of the concentration, to the specific
15 intended use. The fact however that substantially the same mixtures may be used in various steps of the process and that these mixtures are reprocessable brings an important contribution to an overall safer and more reliable process.

 Other objects and advantages of the present inven-
20 tion will appear to those skilled in the art from the detailed description of the invention to follow.

Main characteristic features of the invention

 In order to achieve the intended aims, especially for semiconductor processing, the present invention proposes
25 the use in the liquid phase of mixtures of hydrogen fluoride and one or more carboxylic acids, possibly in admixture with water.

 The carboxylic acid which is used is generally acetic acid (HAc). However, other carboxylic acids having one
30 or more carboxylic functional groups ($-\text{COOH}$) have similar properties and may be used.

 Some higher carboxylic acids, while having very similar properties may be better choices having regard to their dissociation constant.

35 The molar ratio between HF and the carboxylic acid may vary between 1/1000 and 100/1.

When water is present, the concentration of the acids (HF and carboxylic acid) is generally comprised between 0.01 and 25 mol/l.

The specific molar ratio HF/carboxylic acid and the
5 HF acid concentration is typically 1/5 and 2 mol/l HF in etching techniques of SiO₂ and is typically 1/20 and 0.5 mol/l HF for last step cleaning operations.

In order to reduce particulate contamination, isopropyl alcohol (IPA) is preferably added to the mixture
10 composition. Molar ratio ranges of IPA to the total of HF and carboxylic acids between 1/100 and 5 are particularly suitable.

Brief description of the drawings

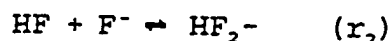
In order to further illustrate its advantages, the present invention will be described in the following description to be read in conjunction with the accompanying
5 drawings.

In these drawings:

- 10 - Figure 1 is a diagram of the etch rate ($E R$ in $\text{\AA}/\text{min}$) as a function of the total fluoride concentration (Conc in mol/l) for HF with and without addition of HCL.
- Figure 2 is a diagram of the relative etch rate ($R E R$ in $\text{\AA}/\text{min}$) as a function of the total fluoride concentration (Conc in mol/l) of figure 1.
- 15 - Figure 3 is a diagram of the relative etching rates (as a function of total fluoride concentration) of the different components of figure 1.
- Figure 4 is a diagram of the absolute etch rate ($E R$ in $\text{\AA}/\text{min}$) as a function of the total fluoride concentration (Conc in mol/l) in a HF/10% HAC solution.
- 20 - Figure 5 is a diagram of the time evolution of the etch depth (d in \AA) as a function of time (t in min) for a 2 M HF/HAC solution.
- 25 - Figure 6 is the histogram of an electrical field breakdown test (normalized frequency f in % in function of E_{bd} in MV/cm) of oxides after stripping with acetic acid/HF (without H_2O).
- Figure 7 is the histogram of an electrical field breakdown test (normalized frequency f in % in
30 function of E_{bd} in MV/cm) of oxides after stripping with standard buffered HF.
- Figure 8 is the histogram of an electrical field breakdown test (normalized frequency f in % in
35 function of E_{bd} in MV/cm) of oxides after stripping with 0.5% HF in H_2O .

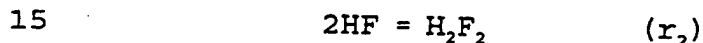
5 Detailed description of the preferred embodiments of the invention

In dilute HF solutions, the following equilibria are well established:



10 For the equilibrium constants K_1 and K_2 of respectively reaction r_1 and r_2 , the values of 6.85×10^{-4} mol/l and 3.693 l/mol are often reported.

For the dimerisation reaction of HF the equilibrium constant K_3 for the reaction



is $K_3 = 2.7$ l/mol.

From these known equilibrium constants, together with the mass law and charge conservation laws, the composition of the solutions can be calculated. The different
20 species are HF, F^- , HF_2^- , H_2F_2 and H^+

The present invention is based upon the observation that due to dissociation constant values of HCl, when adding HCl to HF, the only species present are HF and H_2F_2 .

Fig. 1 expresses the etch rate (R) in Å/min versus
25 the total fluoride concentration in mol/l at various dilution of HF alone and HF/HCl mixtures with a constant HCl concentration of 0.5 mol/l.

In order to study the etching mechanism, it is better to plot the relative etch rate, which means the etch rate divided by the fluoride concentration. This represents
30 the etch rate per mol of fluoride as a function of the total fluoride atom concentration. This is shown in fig. 2 for HF-water diluted solutions and HF/HCl-water diluted solutions which are similar to those of fig. 1.

35 Especially from fig. 2, it can be seen that the etch rate of the HF/HCl solution is much more reproducible than the etch rate of the HF solution.

In such case, the etch rate of every component can be determined by fitting the etch rate as a function of the composition.

The etch rate of the HF/HCL solution can be modelled by the following formula:

$$R = 257 [H_2F_2] + 55.3 [H_2F_2]^2$$

The etch rate of the HF solution can be modelled by the following formula:

$$R = 257 [H_2F_2] + 55.3 [H_2F_2]^2 + 1282 [HF_2^-] + 388.8 * [HF_2^-] * \log([H^+] / [HF_2^-])$$

From this formula it is clear the two species H_2F_2 and HF_2^- are active.

The relative importance of these two species is shown in fig. 3.

From this figure and from the comparison with fig. 2 it can be concluded that the irreproducible etch rates in the HF solution are a result from the irreproducible contribution of the HF_2^- species.

In buffered HF the etching is only due to the HF_2^- molecule since the pH of these solutions is much higher than in diluted HF and at those pH values, only HF_2^- is present.

In buffered HF, the etch rate is modelled as:

$$R = 1282 [HF_2^-] + 388.8 * [HF_2^-] * \log([H^+] / [HF_2^-])$$

In these solutions, the etch rate is still quite reproducible because of the high etch rates in these solutions. Indeed, an irreproducible etching mechanism becomes reproducible at high etch rates because of the statistical smoothening.

However the use of HCL in admixture with HF, instead of the NH_4F /HF mixtures of the so-called buffered HF cannot be contemplated in view of the fact that the HCL etches the silicon (Si) and in this way roughens its surface.

The present invention is based on the consideration that the good reproducibility of the etching operation may be obtained by use in the liquid phase of the new mixtures of the present invention comprising carboxylic acid mixed with HF and possibly water.

Among the various carboxylic acids, acetic acid is a good choice regarding Ca solubility, melting point (17°C),

boiling point (118°C) and dissociation constant ($1.76 \cdot 10^{-5}$). However, other already mentioned carboxylic acids have very similar properties and some are better choices regarding the dissociation constant as will be shown later.

5 The H₂O can be added to enhance the etch rates or to reduce the amount of used carboxylic acid.

 It should be kept in mind that the mixtures according to the present invention may also include various other additives in order to improve specific properties. The
10 mixtures may e.g. include as already mentioned isopropyl alcohol in order to reduce particulate contamination but also ingredients to enhance etching properties or in order to yield better performance such as H₂O₂ (hydrogen peroxide) etc.

15 Fig. 4 and 5 illustrate as an example the etching behavior of mixtures in accordance with the invention.

 Both figures indicate that the etching behavior is very reproducible. This is because in this mixture, as in the HF/HCl mixture, there is no etching due to the HF₂- component
20 since this is absent in these solutions.

 The etch rates as a function of total fluoride concentration is shown in fig. 4 for a 10% acetic acid/H₂O mixture at various HF concentrations.

 The etch depth as a function of time is shown in
25 fig. 5 for a 10% acetic acid/H₂O mixture with 4% HF added (equivalent to 2 mol/l).

 Because the etch depth increases linearly with time, it can be concluded that no depletion is present and that the etching process is very constant.

30 The surface tension of these mixtures is much lower than that of standard buffered HF. E.g. the surface tension of 10% acetic acid/H₂O is 54,60 mN/m while that of standard buffered HF is around 72 mN/m. If less H₂O is used or if a pure acetic acid/HF solution (without H₂O) is used, then the
35 surface tension is even lower. The surface tension of pure acetic acid is 27.7 mN/m.

 The electrical properties of oxides grown on surfaces where the oxide is stripped with acetic acid/HF

mixtures are much better than after stripping the oxide with buffered HF. The histogram of an electrical field breakdown test of oxides after stripping with acetic acid/HF shown in fig. 6, in comparison to the corresponding histogram after stripping with buffered HF shown in fig. 7 and stripping with 0.5% HF in H₂O shown in fig. 8 illustrate clearly that the oxides grown on surfaces after stripping the oxide with acetic acid/HF are superior to those stripped with BHF.

Since in the future, the environmental restrictions on the use of chemicals will be much stricter, it is important to use reprocessable mixture. No commercial workable method is available to reprocess standard buffered HF and the HF depleted solution must be rejected as waste products causing potential pollution hazards to the environment.

Since acetic acid has a very low dissociation constant, it can be reprocessed over an ion exchange resin, using well known techniques of the art.

Ca⁺⁺ is a very important and cumbersome impurity, since it is the metal which has the most detrimental impact on the gate oxide integrity and unfortunately, the solubility of Ca⁺⁺ in HF solution is very low. The addition of carboxylic acid according to the invention improves the solubility of Ca⁺⁺ in HF/carboxylic acid solutions and avoids thus the outplating of Ca on the surface of the Si wafers which are being treated. The solubilities are shown in table I for selected Ca compounds in different environments for which the data is available. From this table it is clear that CaF₂ is much less soluble than CaCl₂ or calcium acetate (CaAc₂).

Although CaCl₂ is very soluble, HCl cannot be used as an additive to HF since HCl would, as already mentioned, etch the Si and in this way roughen its surface.

It is also clear from table I that other carboxylic acids have also a high solubility for Ca⁺⁺ compounds. Some have an even higher solubility than acetic acid, e.g. propionic acid.

A further consideration in the choice of a specific carboxylic acid is the dissociation constant of the intended compound.

Ideally, the dissociation constant should be slightly higher than the dissociation constant of HF. In this way, the formation of HF_2^- is already suppressed when amounts are added which are equal to the HF concentration. At the same time, the dissociation constant should not be too large in order not to lose too much of the product when reprocessing the mixture over an ion exchange bed. Table 2 gives dissociation constants available from the literature.

When taking these considerations into account, the following acids are good choices: iodoacetic acid, bromoacetic acid and chloroacetic acid.

When using acetic acid, large amounts are needed in order to suppress the formation of HF_2^- (amounts typically in excess of 10%). When using e.g. chloroacetic acid, much lower amounts are needed.

In accordance to the invention, other ingredients may be added to the composition of the invention. Especially in order to reduce the particulate contamination, IPA can be added to the mixture carboxylic acid/HF. This is shown in table 3 in the case of acetic acid. From this table, it is clear that the addition of IPA reduces the particle adhesion.

In table 4, it is clear that a 100% acetic acid/HF solution has lower particle adhesion than a 10% acetic acid/HF solution.

Table 1

Solubility of CaF in 0.5% HF, of CaF in H₂O and of
Ca(C₂H₃O₂)₂, CaAcetate) in H₂O

5		Solubility (ppb-weight of Ca)
	CaF in 0.5% HF	97
	CaF in H ₂ O	16*10 ³
	CaCl in H ₂ O	745*10 ⁵
	CaAcetate in H ₂ O	374*10 ⁵
10	CaCitrates in H ₂ O	0.85*10 ⁶
	CaCinnamate	2.2*10 ⁵
	Calcobutyrate	200*10 ⁵
	Capropionate	490*10 ⁵

15

Table 2

Dissociation constant of various acids

		Dissociation constant
	HF	6.85*10 ⁻⁴
	Acetic Acid	1.76*10 ⁻⁵
20	Iodoacetic Acid	7.5*10 ⁻⁴
	Bromoacetic Acid	2.05*10 ⁻³
	di-Chloroacetic Acid	1.4*10 ⁻³
	tri-Chloroacetic Acid	3.32*10 ⁻²
	Formic Acid	1.77*10 ⁻⁴
25	Propionic Acid	1.23*10 ⁻⁵
	Citric Acid	7.4*10 ⁻⁴

Table 3

Particles > 0.3 mm/125 >mm wafer after HF(0.5%)/HOAc(10%)
and HF(0.5%)/HAc(10%)/IPA(1%)

5

HF(0.5%)/HAc(10%)	986
	5.114
	753
	945
	317
HF(0.5%)/HAc(10%)/IPA(1%)	418
	307
	192
	148
	176

Table 4

Particles > 0.3 mm/125 mm wafer after HF(2%)/HAc(100%)

10

HF(2%)/HAc(100%)	151
	85
	244
	274
	322

CLAIMS

1. Method for semiconductor processing comprising etching of oxide layers, especially etching thick SiO_2 layers and/or last step in the cleaning process wherein the
5 oxide layers are treated in the liquid phase with a mixture of hydrogen fluoride and one or more carboxylic acids, possibly in admixture with water.

2. Method according to claim 1 wherein the carboxylic acid is acetic acid.

10 3. Method according to claim 1 wherein the carboxylic acid is a monocarboxylic acid or a multicarboxylic acid having a dissociation constant higher than the dissociation constant of acetic acid.

4. Method according to any one of the claims 1-3
15 wherein the molar ratio between HF and the carboxylic acid is comprised between 1/1000 and 100/1.

5. Method according to any one of the claims 1-4 wherein water is present and wherein the concentration of the acids (HF and carboxylic acid) is comprised between 0.01 and
20 25 mol/l.

6. Method according to any one of the claims 1-5 wherein the specific molar ratio HF/carboxylic acid and the total acid concentration is 1/5 and 2 mol/l HF in etching techniques of SiO_2 and is 1/20 and 0.5 mol/l HF for last step
25 cleaning operations.

7. Method according to any one of the claims 1-6 wherein isopropyl alcohol (IPA) is added to the mixture composition, preferably in molar ratio ranges of IPA to the total of HF and carboxylic acids comprised between 1/100 and
30 5.

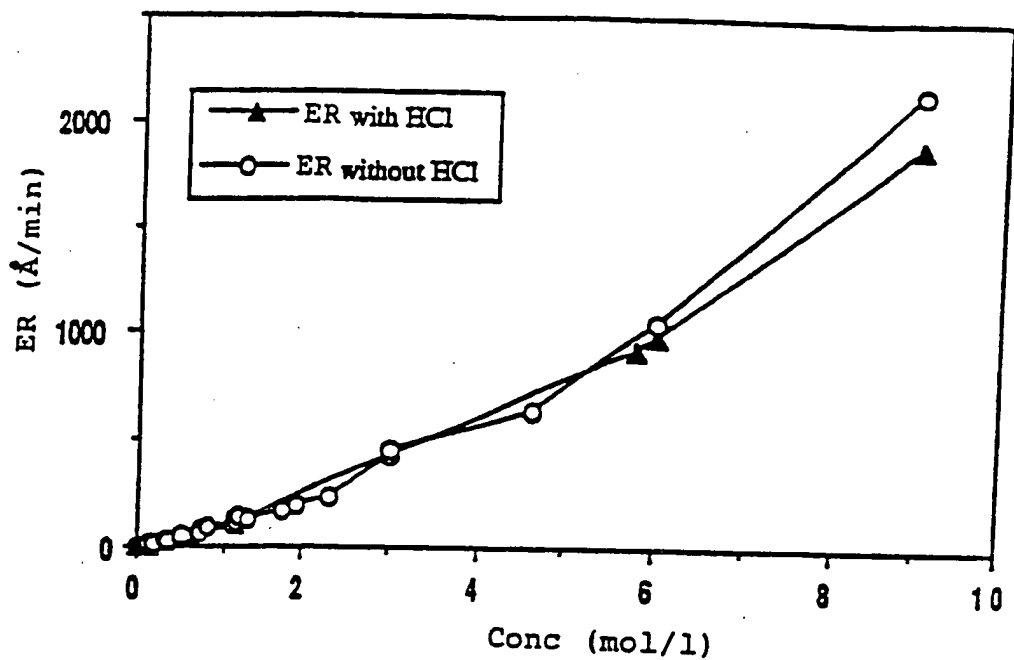


Fig. 1

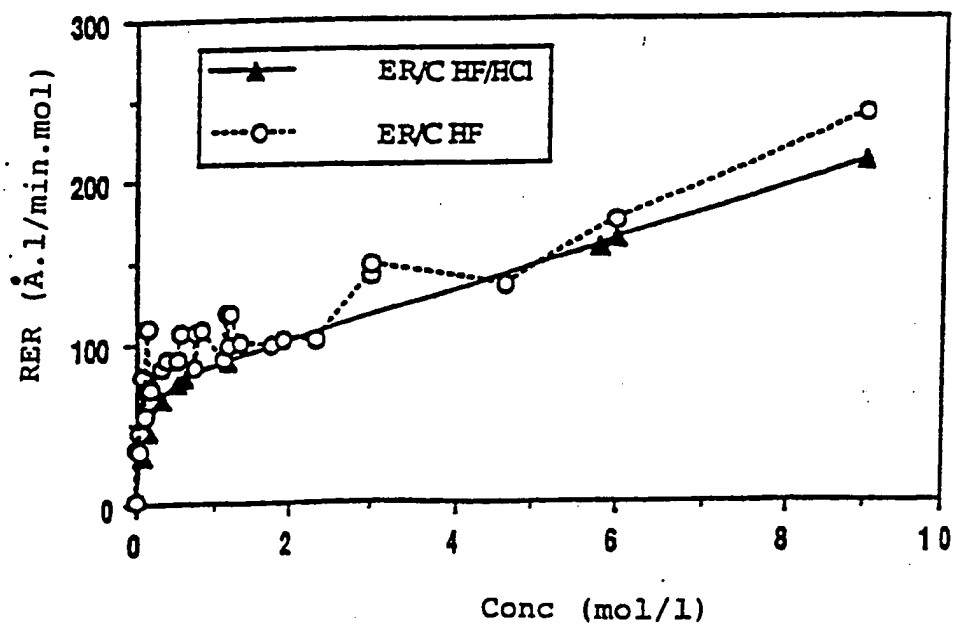


Fig. 2

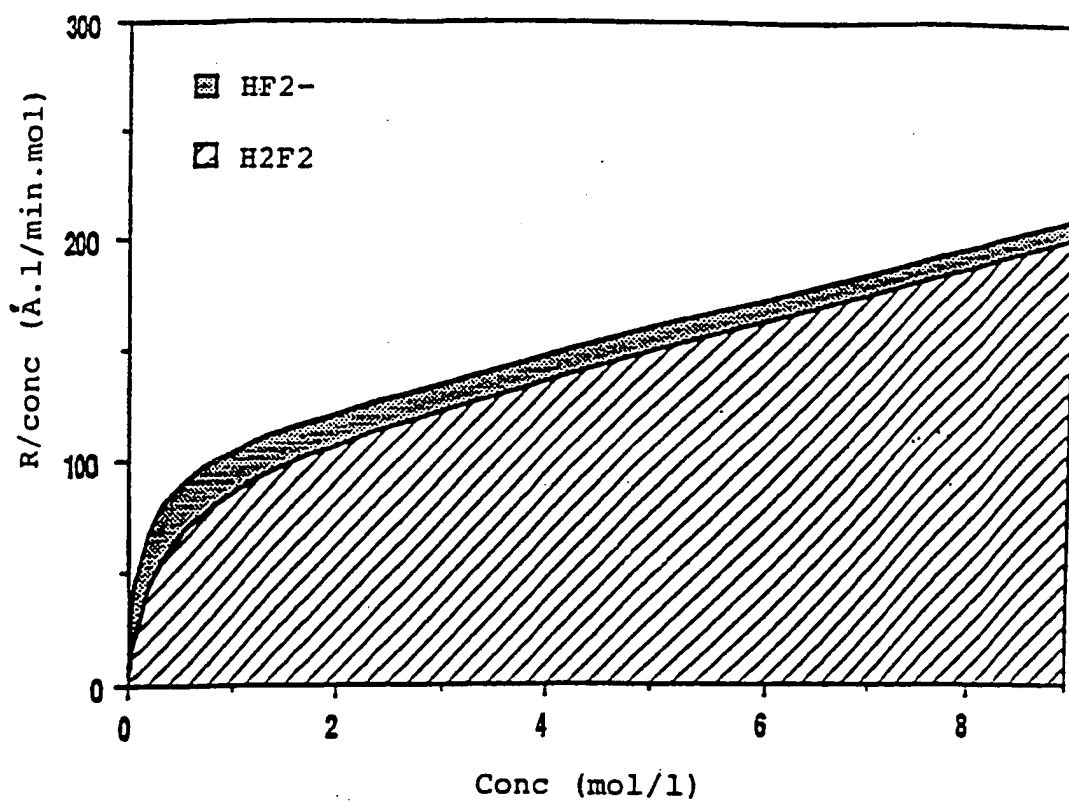


Fig. 3

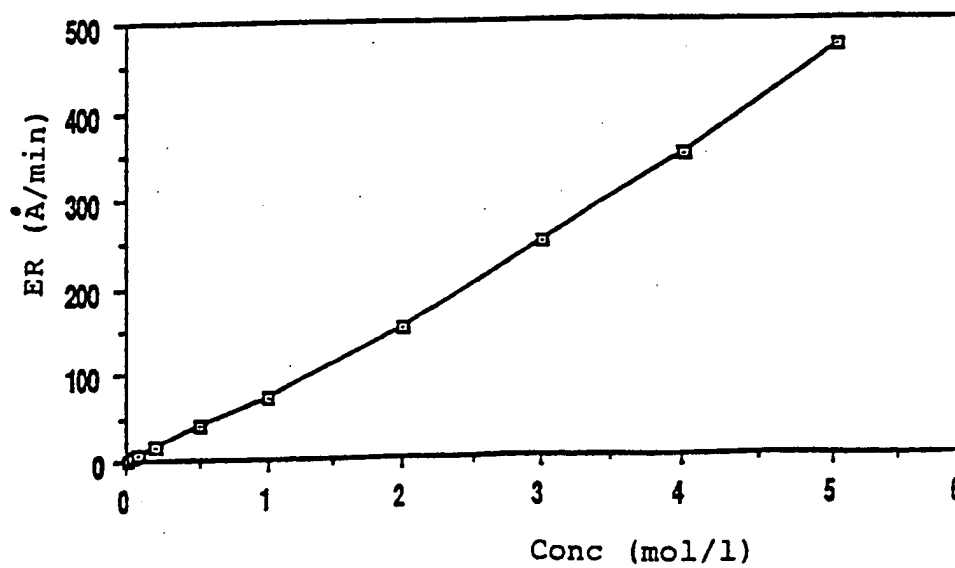


Fig. 4

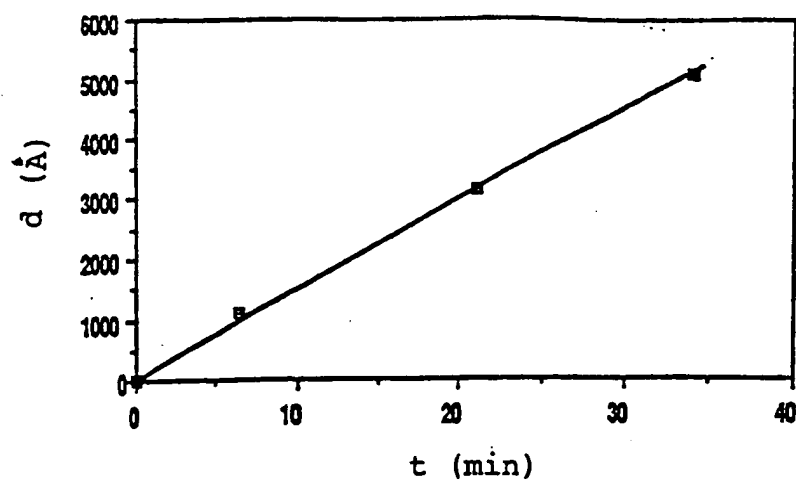


Fig. 5

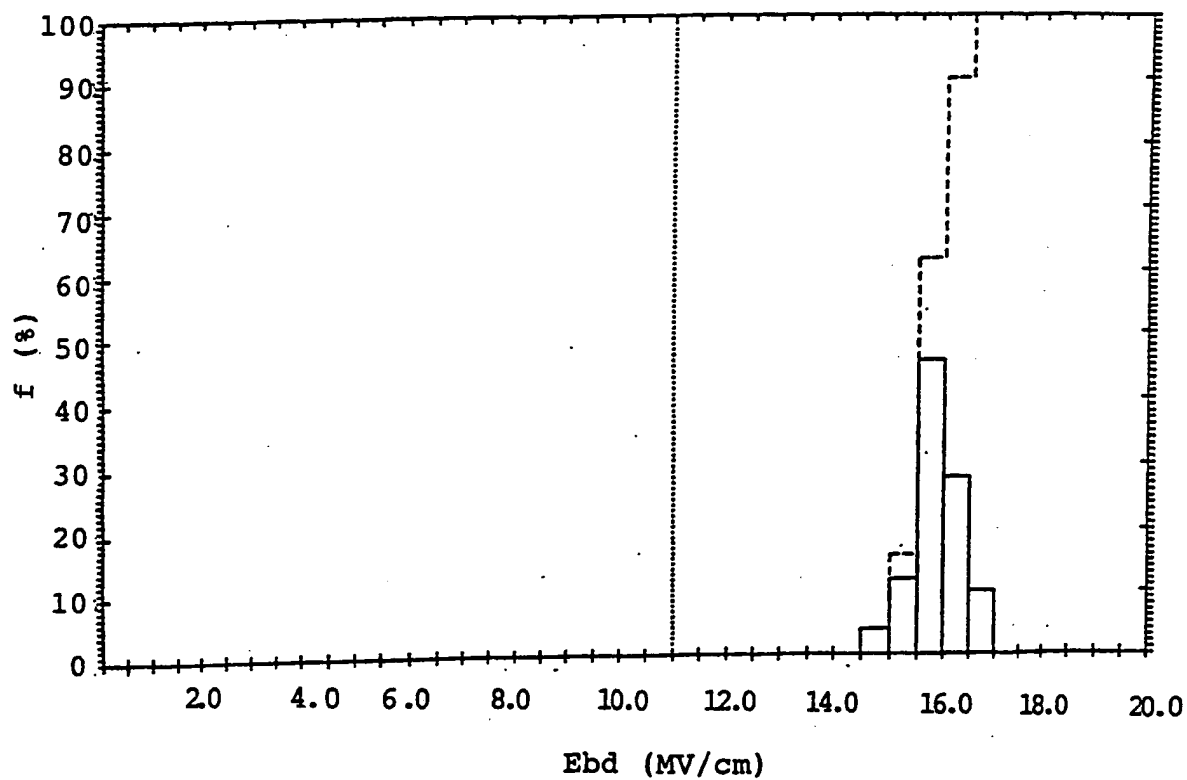


Fig. 6

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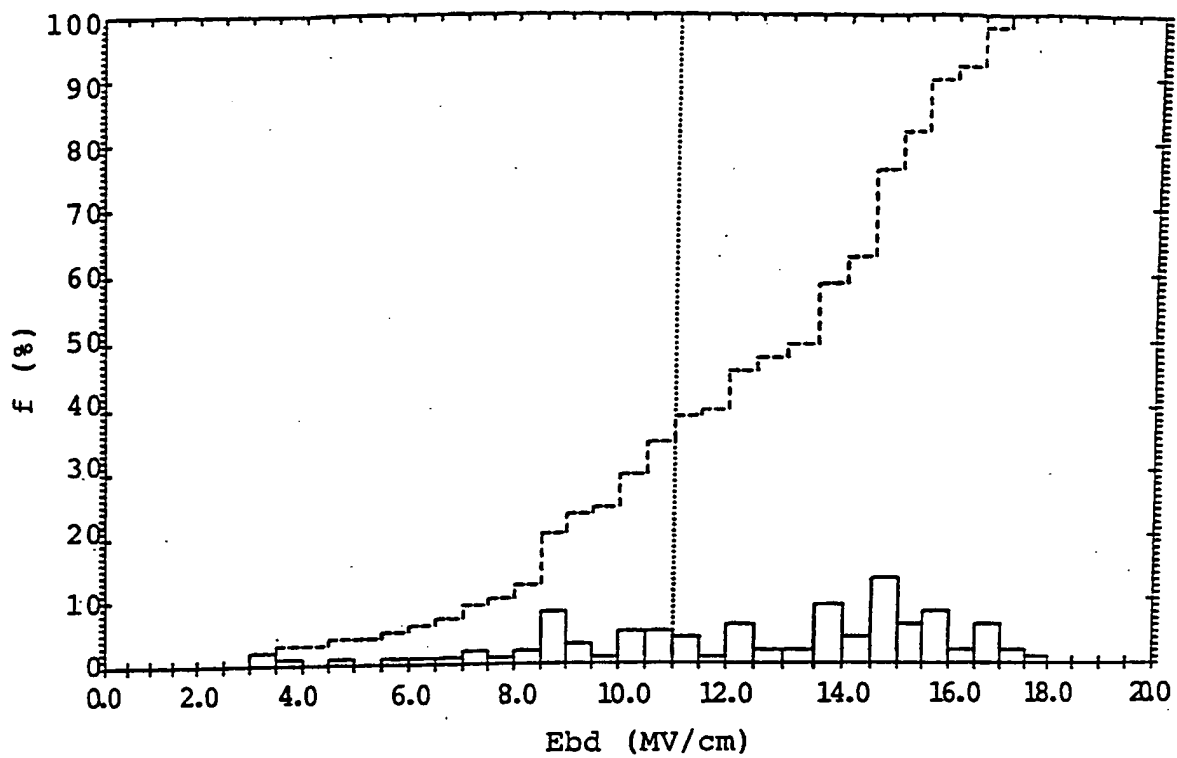


Fig. 7

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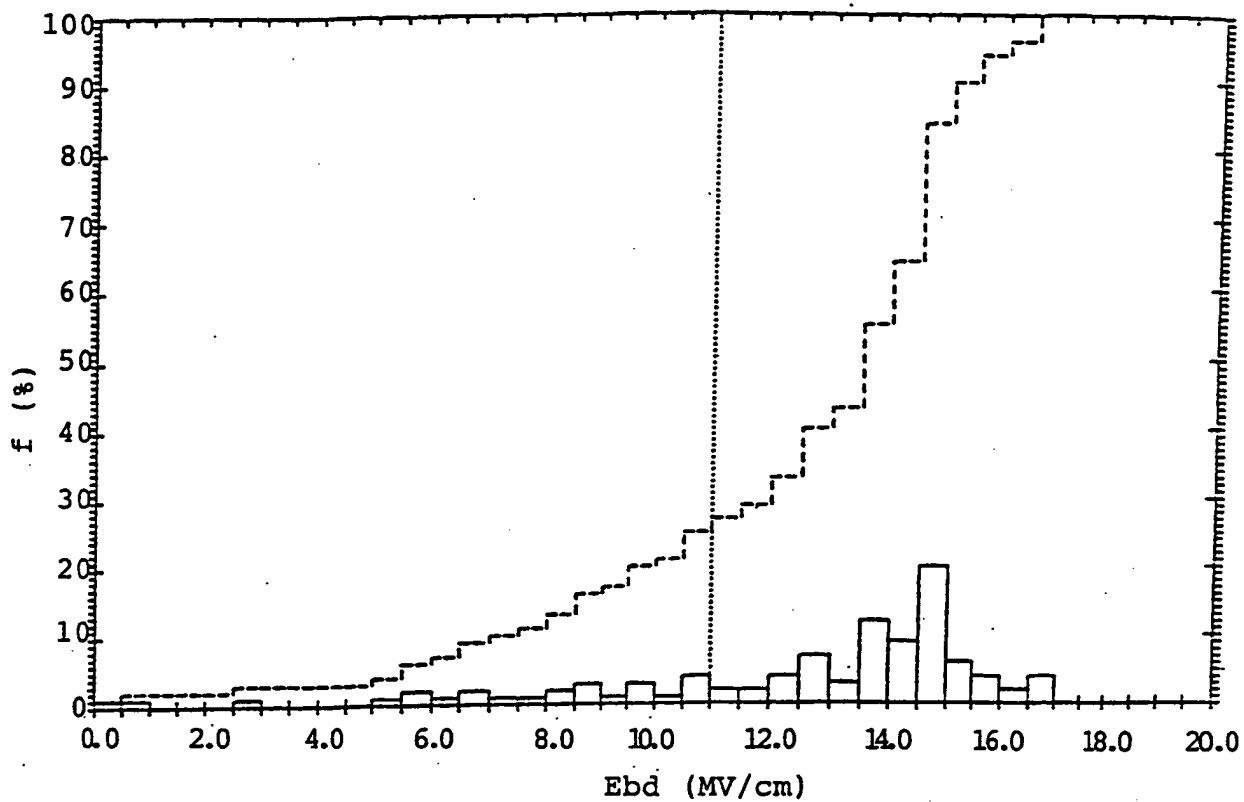


Fig. 8

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 H01L21/311 H01L21/306

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 395 304 (KERN ET AL) 26 July 1983 cited in the application see claims; table 1 ---	1-6
X	EP,A,0 438 727 (SCHNEGG ET AL) 31 July 1991 cited in the application see page 4, line 8 - line 11; claim 1 ---	1,4
P,X	EP,A,0 560 324 (SUGIHARA ET AL) 15 September 1993 see claims ---	1,4,5
A	EP,A,0 477 504 (FLEMING ET AL) 1 April 1992 see claims 1,3,5 ---	1-6
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	IBM TECHNICAL DISCLOSURE BULLETIN., vol.22, no.3, August 1979, NEW YORK US page 1047 HOFFMEISTER ET AL 'Method of reducing surface tension of buffered hydrofluoric acid by adding isopropanol' see the whole document ---	7
A	EP,A,0 133 584 (NAONORI ET AL) 27 February 1985 see claim 1 ---	1
A	US,A,4 885 056 (HALL ET AL) 5 December 1989 see abstract -----	1

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4395304	26-07-83	NONE	
EP-A-0438727	31-07-91	DE-A- 4002327 JP-A- 4212420 US-A- 5051134	01-08-91 04-08-92 24-09-91
EP-A-0560324	15-09-93	JP-A- 6112178	22-04-94
EP-A-0477504	01-04-92	JP-A- 4234118 US-A- 5294570	21-08-92 15-03-94
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US-A-4885056	05-12-89	NONE	